

## PATENT ABSTRACTS OF JAPAN

(11)Publication number : 2002-086476 ○

(43)Date of publication of application : 26.03.2002

(51)Int.Cl.

B29C 41/28  
B01D 67/00  
C08J 9/28  
// B29K105:04  
B29L 7:00  
C08L 79:08

(21)Application number : 2000-284651

(71)Applicant : UBE IND LTD

(22)Date of filing : 20.09.2000

(72)Inventor : YAO SHIGERU ○

OYA NOBUO

FUJII YUICHI

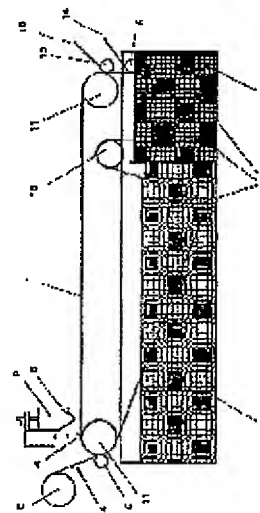
ASANO YUKIHIKO

## (54) METHOD AND APPARATUS FOR CONTINUOUSLY MANUFACTURING POROUS FILM

## (57)Abstract:

**PROBLEM TO BE SOLVED:** To provide a method and apparatus for continuously manufacturing a porous polymer film industrially, capable of homogenously controlling porous characteristics such as film thickness, a pore size, voids, a pore shape or the like.

**SOLUTION:** A polymer solution with a solution viscosity of 10-30,000 poise is supplied on a belt conveyor to form a polymer solution cast film and, after the film thickness of this cast film is uniformly adjusted, a solvent substitution speed adjusting material is continuously supplied to be laminated on the polymer solution cast film. The laminate, which is constituted of the belt conveyor, the polymer solution cast film and the solvent substitution speed adjusting material, is immersed in a coagulation liquid comprising a non-solvent with respect to the polymer and moved through the coagulation liquid to precipitate the porous polymer film, and the laminate is immersed in a structure stabilizing solvent. While the laminate is immersed in the structure stabilizing solvent or after the laminate is taken out of the structure stabilizing solvent, the solvent substitution speed adjusting material and the porous polymer film are peeled from the laminate and the peeled porous polymer film is dried and/or heat-treated to continuously manufacture the porous film of which the porous characteristics such as film thickness, a pore size, voids, a pore shape or the like are homogenous.



\* NOTICES \*

JPO and INPIT are not responsible for any damages caused by the use of this translation.

- 1.This document has been translated by computer. So the translation may not reflect the original precisely.
- 2.\*\*\* shows the word which can not be translated.
- 3.In the drawings, any words are not translated.

DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention]This invention is the method that a polymer porous membrane can be obtained with a phase-shift method while adjusting solvent substitution speed from the flow casting film of a polymer solution, Especially variation is related with the manufacturing method and manufacturing installation of a porous membrane which can obtain continuously the porous membrane which has little penetrated homogeneous porous characteristic.

[0002]

[Description of the Prior Art]The porous polymer film is broadly used for the raw material of industrial materials, such as a filter, a demarcation membrane, and a separator for cells, and a medical material, the optical material, the electronic industry material, etc. How to form [ to carry out extraction removal of said non-subtlety granular powder object or the organic liquefied object, for example, after the manufacturing method of a porous polymer film mixes a non-subtlety granular powder object and an organic liquefied object to polymer and produces a film to it, and ] fine pores, How to form fine pores by performing annealing treatment, forming a lamellae laminated structure in a size enlargement thing, ranking second and extending it in it, making between this lamellae lamination crystal exfoliate, and growing up fibril, after carrying out size enlargement of the crystalline polymer, The phase-shift method etc. in which fine pores are made to form using the phase separation phenomenon which casts a polymer solution, immerses it in solidified solutions (as insoluble in polymer the organic solvent which has compatibility as the solvent of a polymer solution, water, etc.), and is produced in that case occur.

[0003]Said phase-shift method is suitably used, when manufacturing a porous membrane from polymer, such as cellulose acetate, polysulfone, polycarbonate, polyvinyl alcohol, polyamide, polyimide, and polyvinylidene fluoride. However, since the porous membrane obtained with a phase-shift method was an asymmetric membrane by which the dense layer was formed in the outermost surface and fine pores were formed in the inside of a film, the use of the obtained film was limited to the gas separation membrane etc.

[0004]After carrying out the cast of the polyamic acid solution to JP,11-310658,A, a porosity film is laminated to it, and the manufacturing method of the polyimide porous membrane by which this layered product being immersed in a poor solvent is indicated. According to this method, the polyimide porous membrane which has a breakthrough about 0.01-10 micrometers in diameter was able to be obtained. In the aforementioned various uses, the porous membrane which has the penetrated micropore which is obtained by this method is very useful.

[0005]

[Problem(s) to be Solved by the Invention]In the method of obtaining the porous

membrane shown in said JP.11-310658,A, this invention is providing the continuous production method and continuous fabrication device of an industrial porous membrane which can control homogeneously the porosity characteristics, such as thickness, an aperture, a void content, and pore shape.

[0006]

[Means for Solving the Problem]A process of this invention supplying a polymer solution whose solution viscosity is 10-30000 poise on a band conveyor for the purpose of solving an above-mentioned technical problem, and forming a polymer solution flow casting film, A process of adjusting said polymer solution flow casting film to uniform thickness, and a process which supplies solvent substitution speed-regulation material continuously, and is stuck on said polymer solution flow casting film, A process which immerses into a solidified solution containing a non solvent [ as opposed to said polymer for a layered product which consists of a band conveyor a polymer solution flow casting film, and solvent substitution speed-regulation material which were formed at said process ], and moves inside of a solidified solution, and deposits a porous polymer film, A process that said layered product is immersed into a structural stability-ized solvent, and a process of exfoliating solvent substitution speed-regulation material and a porous polymer film from said layered product after taking out under immersion or from said structural stability-ized solvent in said structural stability-ized solvent, It is related with a continuous production method of a porous membrane constituted including desiccation and/, or a process to heat-treat in said exfoliative porous polymer film, A band conveyor which can drive this invention and a feed zone which supplies a polymer solution, A film-thickness-adjusting part of a polymer solution flow casting film, and a feed zone and a lamination part which supply solvent substitution speed-regulation material continuously, and are stuck on said polymer flow casting film, It is constituted including a solidified solution tub and a structural stability-ized solvent tub, and a stripping part of solvent substitution speed-regulation material and a porous polymer film, After forming a polymer solution flow casting film of homogeneous thickness on a band conveyor, on said flow casting film, stick solvent substitution speed-regulation material and a layered product is formed, Subsequently, it is related with a continuous fabrication device of a porous membrane constituted so that said layered product might be immersed in a solidified solution, and inside of a solidified solution might be moved and a porous polymer film might be deposited.

[0007]

[Embodiment of the Invention]A continuous fabrication device given in the continuous production method and this application claims 7-10 of a porous membrane given in this application claims 1-6 has a relation corresponding to mutual so that each composition of each may state below.

[0008]The continuous production method of the porous membrane of this invention is explained. Polymer is uniformly dissolved into a solvent and a polymer solution is deaerated enough. The polymer concentration of said polymer solution is 1 to 30 % of the weight preferably 0.3 to 60% of the weight. At less than 0.3 % of the weight, since control of a deposit of polymer will become difficult if 60 % of the weight is exceeded undesirably, since the intensity of the porous membrane obtained falls, it is not desirable. 10-30000 poise of solution viscosity [ 50-10000 poise of ] (rotation viscosity) of a polymer solution is 100-5000 poise especially preferably preferably. Since it will become difficult it to become difficult to make it cast easily on a band conveyor, or to adjust thickness uniformly, and for control of solvent substitution speed to become difficult, and to control homogeneously the porosity characteristics, such as an aperture, a void content, and pore shape, if solution viscosity exceeds 30000 poise, it is not suitable. Since it becomes impossible to hold the shape as a flow casting film in less than 10 poise, and it is easy to

produce thickness nonuniformity and it has become, it is not suitable. In order to obtain uniform thickness, it is preferred for said polymer solution to be supplied on a band conveyor with constant flow. Since the method of extruding a polymer solution from a nozzle (T die) by pressurizing the inside of the feed unit in which the polymer solution was stored as a feeding method at a fixed pressure using a gas especially dry air, or inactive gas can prevent mixing of air bubbles etc., it is desirable. As for a polymer solution, it is preferred to be supplied by the T die with constant flow with fixed width on a band conveyor.

[0009]As for a band conveyor, what has the detachability which can remove easily the porous membrane in which it is smooth and the surface deposited is preferred. Since endurance needs to be excellent even if it contacts an organic solvent, a metal belt, especially the belt made from stainless steel are preferred. A band conveyor is what can change speed, and that from which change becomes the degree of constant speed few is preferred for it during a drive.

[0010]As for the polymer solution flow casting film cast on the band conveyor, thickness is adjusted. Although adjustment of thickness is suitably performed by the braid (doctor knife) which is installed so that it may have a uniform crevice a band conveyor and crosswise, for example, and can adjust the crevice, Since it is necessary to adjust thickness with sufficient accuracy uniformly, it is preferred to be carried out by the part which the belt undersurface supports with the roll or the plate. In the method of this invention, 1-2000 micrometers of polymer flow casting thickness are especially adjusted to 10-500 micrometers preferably. The intensity of the porous membrane which will be obtained if thickness is smaller than 1 micrometer becomes less enough, and is not preferred. Since it becomes difficult to control homogeneously the porosity characteristics, such as an aperture, a void content, and pore shape, since the homogeneity of the porous structure of the thickness direction of the porous membrane which will be obtained if thickness exceeds 2000 micrometers worsens, it is not desirable.

[0011]Subsequently, solvent substitution speed-regulation material is stuck on said polymer solution flow casting film. In the case of this lamination, it is preferred that a pressure is controlled so that the thickness of a polymer solution flow casting film does not change substantially. Not changing substantially are not less than 90% of thickness, and sticking it preferably, as not less than 95% of thickness is held to the thickness of the polymer flow casting film before being stuck. Since it will become difficult to control homogeneously the porosity characteristics obtained by a polymer solution's flowing compulsorily and the variation in flow casting thickness becoming large, such as thickness of a porous membrane, an aperture, a void content, and pore shape, if a pressure when sticking is high, it is not desirable.

[0012]Although the lamination of said solvent substitution speed-regulation material moves the polymer solution flow casting film on a band conveyor to an abbreviated horizontal direction and does not matter that it is \*\*\*\*\*, the polymer solution flow casting film on a band conveyor -- an abbreviated perpendicular direction -- or, moving a polymer solution flow casting film below to a perpendicular direction at the angle of 60 degrees or less (from an abbreviated perpendicular to 45 degrees [ Preferably ] or less) by the state where it turned up. Especially since thickness of a polymer flow casting film cannot change easily due to the weight of the solvent substitution speed-regulation material which sticking solvent substitution speed-regulation material on said polymer solution flow casting film stuck, it is suitable. For example, especially the thing for which lamination is performed is preferred while progressing, while the layered product of a band conveyor and a polymer flow casting film changes a direction from an abbreviated horizontal direction to an abbreviated perpendicular direction with a roll.

[0013]The solvent substitution speed-regulation material of this invention is a porosity film, and when it contacts a polymer flow casting film to a solidified solution and deposits polymer, what has the permeability which is a grade which the solvent and solidified solution of a polymer solution can penetrate at a suitable speed is preferred. In particular, that whose air permeability (Gurley value) is 50 to 1000 seconds/100cc, and also 250 to 800 seconds/100cc is preferred. The thickness of solvent substitution speed-regulation material is 5-100 micrometers, and 5-500 micrometers of things which the aperture penetrated in the direction of a film cross section is distributing by 0.01-10 micrometers and desirable density with a 0.03-1-micrometer sufficient hole are preferably preferred for it. Since it becomes impossible to adjust enough solvent substitution speed -- a dense layer is formed in the polymer surface which solvent substitution speed is too quick and deposits -- when the air permeability of solvent substitution speed-regulation material is larger than a mentioned range, are not suitable. If smaller than a mentioned range, solvent substitution speed will become slow too much, and the porous structure formed in deposit polymer will become uneven.

[0014]As solvent substitution speed-regulation material, specifically Polyolefines, such as polyethylene and polypropylene, Since it excels in the smooth nature of the film surface of the manufactured porous membrane when a nonwoven fabric or a porous membrane made from cellulose, Teflon (registered trademark), etc. is used and the fine porous membrane made from polyolefine is used especially, it is suitable.

[0015]In this invention, the layered product on which a band conveyor, a polymer flow casting film, and solvent substitution speed-regulation material were stuck is immersed in a solidified solution, and the inside of a solidified solution is moved, and a porous polymer film is deposited. In a solidified solution, a non solvent contacts a polymer solution flow casting film via solvent substitution speed-regulation material, and is gradually replaced by the solvent in a polymer solution flow casting film, and, in the phase separation of a polymer solution flow casting film, a \*\*\*\*\* porous polymer film deposits. If the substitution of this solvent and a non solvent inclines and it is carried out that there is nothing, the porosity characteristics obtained, such as thickness of a porous membrane, an aperture, a void content, and pore shape, can be made homogeneous. Thickness of a porous membrane, an aperture, a void content, pore shape, etc. which are acquired since the progress condition of phase separation will not become homogeneous, if variation arises in the substitution of a solvent and a non solvent become heterogeneous. One of the features of this invention is in depositing a porous polymer film, moving said layered product in a solidified solution, and making the solvent which touches said layered product surface always refresh. Namely, the concentration of the local solvent and non solvent which happen when the solvent in a polymer flow casting film and the non solvent in a solidified solution replace, The porosity characteristics obtained, such as thickness of a porous membrane, an aperture, a void content, and pore shape, are controlled more to homogeneity by controlling by always refreshing the solvent which touches the surface in the bias of a presentation, inclining and advancing substitution of a solvent and a non solvent that there is nothing.

[0016]In this invention, the speed, i.e., the speed of a band conveyor, which makes the layered product on which a band conveyor, a polymer flow casting film, and solvent substitution speed-regulation material were stuck advance into a solidified solution has preferred 0.01-m 50-m part for /- and thing [ a part for /]. By 0.01-m/, in the following, since productivity is bad, it is not suitable, and if a part for 50-m/is exceeded, since a device will become large too much and a problem will arise in control of belt driving, management of a solidified solution (coagulation tub), etc., it is not desirable.

[0017]As a solidified solution of this invention, the non solvent of said polymer or the

mixed solvent of 99.9 to 40 % of the weight of these non solvents and 0.1 to 60 % of the weight of solvents of said polymer solution can be used. Since the structure of the porous membrane which deposits becomes uniform easily when the mixed solvent which becomes a solidified solution from a non solvent and a solvent is used, it is suitable. Namely, the non solvent used as a solidified solution is a polymer non solvent, and is a thing with the solvent and compatibility of a polymer solution, For example, ether, such as ketone, such as alcohols, such as methanol, ethanol, and isopropyl alcohol, and acetone, and diethylether, water, etc. are used.

[0018]Subsequently, a band conveyor, the porous membrane which deposited, and solvent substitution speed-regulation material are immersed into a structural stability-ized solvent in the state where it stuck. A structural stability-ized solvent removes thoroughly the solvent of the polymer solution which remains in the porous membrane which deposited in said solidified solution, and stabilizes porous structure. Although said solidified solution may have the operation to which the phase separation of a polymer solution is urged and the mixed liquor of a non solvent and a solvent, etc. may be used, a structural stability-ized solvent has a solvent preferred [ compatibility ] in which solubility is not shown to polymer, although it has a solidified solution and compatibility. For example, lower alcohol, hexane, water, etc. can be used conveniently.

[0019]The structural stability-ized solvent also has the effect which promotes exfoliation with a band conveyor, the porous membrane which deposited, and solvent substitution speed-regulation material. Therefore, while being immersed into the structural stability-ized solvent, solvent substitution speed-regulation material and the porous membrane which deposited may be made to exfoliate. Or after taking out out of a structural stability-ized solvent, solvent substitution speed-regulation material and the porous membrane which deposited may be made to exfoliate. If solvent substitution speed-regulation material and a porous membrane are made to exfoliate without being immersed in a structural stability-ized solvent, and desiccation and heat treatment are performed, It is not desirable, in order for porous structure to tend to cause modification and to obtain the uniform porosity characteristic, since stress and heat can be applied into a porous membrane after the solvent of a polymer solution has remained considerably.

[0020]the porous membrane which exfoliated from solvent substitution speed-regulation material and a band conveyor — subsequently — desiccation and/— or it is heat-treated. As for this process, it is preferred to process suitably according to the kind of polymer or the kind of used solvent, respectively. For example, in the porous membrane of polyamic acid, polyimide porous membrane can be eventually obtained by performing and forming high temperature heat treatment in a temperature requirement (200 \*\* – 500 \*\*) into heat imide following 80–100 \*\* hot air drying. In the case of these desiccation and heat treatments, in order to control the heat contraction of the cross direction of a porous membrane, support crosswise both ends by a pin tenter etc., and fixed tension is applied. Since the porous membrane which stabilized porous structure (pore shape, an aperture, etc.) and had uniform porosity can be obtained, it is preferred to carry out to a film by applying fixed tension with a tension roll, in order to control the heat contraction of the lengthwise direction of this film.

[0021]The polymer used in this invention should just be polymer used in the usual phase-shift method, Although cellulose acetate, polysulfone, polycarbonate, polyvinyl alcohol, polyamide, polyimide, polyvinylidene fluorides, those precursors, those mixtures, etc. can be used conveniently, Since it has the characteristic which was extremely excellent in heat resistance, a solvent-proof, \*\*\*\* stability, insulation, etc., it can use that aromatic polyimide or an aromatic polyimide precursor is especially useful and conveniently.

[0022]The case where a polyimide precursor is used as polymer below is explained. With

said polyimide precursor, a tetracarboxylic acid ingredient and a diamine component, They are the polyamic acid produced by polymerizing an aromatic monomer preferably, or its thing which can be imide-ized selectively, can carry out a ring closure by heat imide-ization or forming chemicals imide, and can be made into polyimide resin. The imidization ratio of polyimide resin is not less than about 95% of heat-resistant polymer suitably not less than about 80%.

[0023]The organic solvent used as a solvent of said polyimide precursor, The parachlorophenol, N-methyl-2-pyrrolidone (NMP), pyridine, N,N-dimethylacetamide, N,N-dimethylformamide, dimethyl sulfoxide, tetramethylurea, phenol, cresol, etc. are mentioned.

[0024]In the above-mentioned organic solvent, an aforementioned tetracarboxylic acid ingredient and aromatic diamine component carry out the profile equimolar dissolution, polymerize, and the polyimide precursor whose logarithmic viscosity (30 \*\*, concentration; 0.5g /, 100mL NMP) is especially 0.5-7 0.3 or more is manufactured. When it polymerizes at the temperature of not less than about 80 \*\*, the polyimide precursor which carried out the ring closure selectively and was imide-ized is manufactured.

[0025]As the aforementioned aromatic diamine, it is a general formula (1), for example,  $H_2N-R(R1) m-A-(R2) nR'-NH_2$  (1)

(However, in said general formula, direct coupling or the aromatic ring of bivalence, and R1 and R2 R and R'.) They are substituents, such as a hydrogen, low-grade alkyl, and low-grade alkoxy \*\*, halogen atom, A is a basis of bivalence, such as direct coupling or O, S, CO, SO<sub>2</sub>, SO, CH<sub>2</sub>, and C(CH<sub>3</sub>)<sub>2</sub>, and m and n are the integers of 1-4. The aromatic diamine compound shown is preferred.

[0026]As a concrete compound of said aromatic diamine, 4,4'-diaminodiphenyl ether (it may be hereafter written as DADE), 3,3'-dimethyl- 4,4'-diaminodiphenyl ether, 3,3'-diethoxy- 4,4'-diaminodiphenyl ether, a p phenylenediamine, etc. are mentioned.

[0027]As the aforementioned aromatic diamine component, it may be diaminopyridine and, specifically, 2,6-diaminopyridine, 3,6-diaminopyridine, 2,5-diaminopyridine, 3,4-diaminopyridine, etc. are mentioned. An aromatic diamine component may be used combining each of above-mentioned aromatic diamine components two or more sorts.

[0028]As the aforementioned tetracarboxylic acid ingredient, a biphenyl tetracarboxylic acid ingredient is mentioned suitably, For example, 3,3',4,4'-biphenyl tetracarboxylic dianhydride. Although (it may write as s-BPDA hereafter) 2,3,3',4'-biphenyl tetracarboxylic dianhydride is preferred, They may be the salts or those ester derivatives of 3,3',4,4'-, 2,3,3',4'-biphenyl tetracarboxylic acid, 3,3',4,4'-, or 2,3,3',4'-biphenyl tetracarboxylic acid. A biphenyl tetracarboxylic acid ingredient may be a mixture of each above-mentioned biphenyl tetracarboxylic acid.

[0029]The above-mentioned tetracarboxylic acid ingredient Pyromellitic acid, 3,3',4,4'-benzophenone tetracarboxylic acid, 2,2-bis(3,4-dicarboxyphenyl)propane, a bis(3,4-dicarboxyphenyl)sulfone, It may be tetracarboxylic acid, such as bis(3,4-dicarboxyphenyl) ether, bis(3,4-dicarboxyphenyl)thioethers or those acid anhydrides, a salt, or an esterification derivative. A part of these aromatic tetracarboxylic acid ingredient may be replaced to all the tetracarboxylic acid ingredients at a 10 mol % less or equal, especially a rate not more than 5 mol % with aliphatic series tetracarboxylic acid, such as butanetetracarboxylic acid or those acid anhydrides, a salt, or an esterification derivative.

[0030]The aforementioned polyimide precursor dissolves in said organic solvent at 1 to 30% of the weight of a rate preferably 0.3 to 60% of the weight, and is prepared by the polyimide precursor solution (an organic solvent may be added or a polymerization solution may be used as it is). Since the film strength at the time of producing a porous membrane will fall if the rate of a polyimide precursor is smaller than 0.3 % of the weight, are not



suitable, Since solution viscosity control will become difficult, solution viscosity will become high, flow casting will become difficult, and control of a porous membrane deposit will become difficult, if larger than 60 % of the weight, and it is not desirable, the above-mentioned range is preferred. in the aforementioned polymer concentration, a polymer solution is suitable solution viscosity -- 50-10000-poise 10-30000 poise can be adjusted especially easily [ it is desirable and ] for 100-5000 poise more preferably.

[0031]The porous membrane which consists of a polyimide precursor obtained in this invention method is formed into heat imide by heat-treatment, and is used as polyimide porous membrane. Although chemicals imide-ization can also carry out [ imide ]-izing, since there is a tendency for the intensity of the film obtained to become large in addition to a process not becoming complicated by the method of forming into heat imide, it is suitable. Heat imide-ization can be suitably performed by heat-treating for [ for / 5 minutes / - ] 60 minutes at 250 \*\* - 500 \*\* in the atmosphere as above-mentioned.

[0032]Next, drawing 1 which is a schematic diagram of a typical embodiment - drawing 4 explain the continuous fabrication device of the porous membrane of this invention. The continuous fabrication device of this invention is not limited to the embodiment shown in the schematic diagram of drawing 1 - drawing 4. The continuous fabrication device of this invention is provided with the band conveyor 1 which is speed variable and is driven by constant speed. As for the band conveyor 1, what has the detachability which can remove easily the porous membrane in which it is smooth and the surface deposited is preferred. Since endurance needs to be excellent even if it contacts an organic solvent, a metal belt, especially the belt made from stainless steel are preferred.

[0033]It has the feed zone 2 which supplies a polymer solution with constant flow. This feed zone is held where a polymer solution is deaerated, is constant flow and is supplied on a band conveyor from the nozzle (or T die) 3. the sealed container which stored the polymer solution although supply could be performed using the pump -- a gas -- by the method of pouring in inert gas, such as dry air or nitrogen gas, preferably, and extruding a polymer solution with constant flow with a fixed pressure. It can carry out suitably, without making air bubbles mix. Although the supplying form to a band-conveyor top has the method of extruding from a nozzle, the method of carrying out a spray, etc, and those nozzles traverse crosswise [ of a belt ], what is uniformly supplied crosswise with constant width through the T die which has a slit crosswise [ of a belt ] is preferred. If it carries out like this, even when solution viscosity is comparatively high, the flow casting film of the polymer solution to which thickness was equal can be formed. The formed flow casting film moves with a belt, and has thickness adjusted by the film-thickness-adjusting part 4 in higher accuracy. The film-thickness-adjusting part 4 is constituted by the braid (doctor knife) which placed the fixed crevice and it had to the belt surface. The size of a crevice is variable. In order for the belt undersurface to support by a plinth with a roll or a smooth surface in order to adjust thickness with sufficient accuracy uniformly, and also to prevent play of a belt, it may be constituted so that the undersurface may be attracted and a smooth side may be adsorbed.

[0034]The continuous fabrication device of this invention is provided with the feed zone 5 and the lamination part 6 of solvent substitution speed-regulation material. The feed zone 5 of solvent substitution speed-regulation material is stuck on the polymer solution flow casting film which for example, solvent substitution speed-regulation material was continuously supplied from the supply roll, was guided by the pinch roll in the lamination part 6, and was formed on the band conveyor. Under the present circumstances, even if solvent substitution speed-regulation material is stuck, the crevice between a pinch roll and a band conveyor can be adjusted so that the thickness of a polymer flow casting film may apply the pressure of the grade which does not change substantially. a lamination



part, although the polymer solution flow casting film on a band conveyor is moved to an abbreviated horizontal direction and it may be constituted by obtaining \*\*\*\*\*, the polymer solution flow casting film on a band conveyor — an abbreviated perpendicular direction — or, moving a polymer solution flow casting film below to a perpendicular direction at the angle of 60 degrees or less (preferably 45 degrees or less) by the state where it turned up. If it is constituted so that solvent substitution speed-regulation material may be stuck on said polymer solution flow casting film, especially since thickness of a polymer flow casting film cannot change easily due to the weight of the stuck solvent substitution speed-regulation material, it is suitable. For example, if it is constituted so that lamination may be performed by the part which a band conveyor and a polymer flow casting film are led to a roll, and follow to the abbreviated perpendicular direction from the abbreviated horizontal direction as shown in drawing 1 - drawing 4. Since change of thickness etc. does not take place easily in response to influence due to the weight of solvent substitution speed-regulation material, a polymer solution flow casting film is preferred.

[0035]It is preferred to be constituted so that the humidity and temperature of the space through which the band conveyor 1 from the polymer solution feed zone 2, the film-thickness-adjusting part 4 of a flow casting film, the lamination part 6 of solvent substitution speed-regulation material, and a lamination part to the solidified solution tub 7 passes can be controlled by the continuous fabrication device of this invention. Since temperature affects polymer solution viscosity, it is necessary to control it uniformly. If it does not hold to low humidity when the hygroscopic solvent is used, a solvent will absorb moisture and the problem of becoming it being easy to deposit polymer will arise. Since temperature and humidity affect a phase separation precipitation process, when managing uniformly controls homogeneously the porosity characteristics, such as an aperture, a void content, and pore shape, they are important. As for the air cleanliness class of such space, in order to avoid the influence of dust, it is desirable to have a cleaned device so that it may be held at a required level.

[0036]The continuous fabrication device of this invention is provided with the solidified solution tub 7 and the structural stability-sized solvent tub 8. An above-mentioned solidified solution and structural stability-sized liquid are stored in these tubs, respectively. It comprises this invention so that the layered product which stuck a band conveyor, the flow casting film of a polymer solution, and solvent substitution speed regulation material may be immersed in a solidified solution and it may move in the inside of a solidified solution. The solvent and solidified solution solvent of a polymer solution replace gradually during immersion, phase separation is caused, and a porous membrane deposits. It is very important when replacing these solvents homogeneously controls homogeneously the porosity characteristics, such as an aperture of a porous membrane, a void content, and pore shape. The solvent which moves said layered product in a solidified solution solvent, and touches the layered product surface is made to always refresh, and it comprises this invention so that the bias of local solvent concentration may be controlled. Since immersion needs to be performed enough, you may have two or more these tubs. Like the embodiment of drawing 2, as a layered product moves in a zigzag direction within a solidified solution tub, it may be constituted so that sufficient immersion time may be gained. Since phase separation is influenced with the presentation of temperature or a solvent, it is preferred for a solidified solution tub that management of temperature, solvent composition, etc. is performed enough.

[0037]In the manufacturing installation of this invention, it may be constituted so that said layered product may make it advance into an abbreviated perpendicular to a solidified solution like the embodiment of drawing 1 and drawing 2, and it does not matter even if it

is constituted so that said layered product may incline to the solidified solution surface like the embodiment of drawing 3 and drawing 4 and it may advance into a solidified solution. It constitutes so that a layered product may incline and move to the solidified solution surface like the embodiment of drawing 4 at the process which said layered product advances and moves to a solidified solution, If it constitutes so that a layered product may incline and move to the solidified solution surface also at the process taken out from a solidified solution, Since adjustment of making the water level of a solidified solution high, lengthening immersion time (immersion distance), or making the water level of a solidified solution low and shortening immersion time (immersion distance) can be performed easily, it is very suitable. Since the entry speed to the solidified solution of a layered product also affects it to solvent substitution and a phase separation deposit action, it is desirable for it to be able to adjust in 0.01-m a part for /-, and 50-m the range for /.

[0038]In the manufacturing installation of this invention, although the drive in particular of a band conveyor is not limited and can use the usual drive method, it is suitably performed using a drive roll or a free roll. In a roll as shown by 13 of drawing 1 - drawing 4, since the solvent substitution speed-regulation material of a layered product carries out direct contact to a roll surface, in order to ease the compression stress added to a porous membrane, what covered the roll surface with elastic bodies, such as rubber, is used suitably. Since a porous gestalt may change a porous membrane in response to compression stress in metal, such as stainless steel, the surface of such a roll is not preferred.

[0039]The stripping part 9 of solvent substitution speed regulation material and the stripping part 10 of the porous membrane which deposited may be incorporated so that the structural stability-ized solvent tub 8 may exfoliate solvent substitution speed regulation material and/, or the porous membrane that deposited in a structural stability-ized solvent. In this case, since each exfoliation becomes easy, it is preferred to arrange so that a porous membrane may be exfoliated after exfoliating solvent substitution speed-regulation material first and contacting a solvent to a porous membrane more. The structural stability-ized solvent tub 8, the stripping part 9 of solvent substitution speed regulation material, and the stripping part 10 of a porous membrane may be constituted so that solvent substitution speed regulation material and/, or the porous membrane that deposited may be exfoliated after coming out of a structural stability-ized solvent.

[0040]As for the porous membrane which exfoliated, desiccation and/, or heat treatment is performed. For the purpose, it has an air forced oven and/, or a high-temperature-heat-treatment device. An air forced oven and/, or a high-temperature-heat-treatment device, the porous membrane which united with a polymer feed zone to the stripping part, and exfoliated -- continuous -- desiccation and/-- or it may be constituted so that it may be heat-treated -- an air forced oven and/, or a high-temperature-heat-treatment device may be arranged so that it may carry out or may become another process about desiccation and/, or heat treatment.

[0041]A porous membrane with the porous structure which has especially detailed continuous pores whose void content is 15 to 85%, and whose average pore size is 0.01-10 micrometers preferably by this invention can be obtained. These detailed continuous pores lead in nonlinear, while fine pores are following the shape of a passage to other surfaces and are crooked from the arbitrary surfaces. Even if a void content makes high the porous membrane obtained by this invention, its mechanical strength is high, and since the porosity characteristics, such as thickness, an aperture, a void content, and pore shape, are moreover homogeneous porous membranes, in various uses, it is very useful.

[0042]

[Example]Next, an example explains this invention. However, this invention is not limited to the following examples.

(Reference example)

As an adjustment tetracarboxylic acid ingredient of a polyamic acid solution, s-BPDA, The mole ratio of DADE to S-BPDA is 0.996, and using DADE as a diamine component, it dissolved in NMP so that the total weight of this monomer component might be 10% of the weight, and the temperature of 40 °C and a 6-hour polymerization were performed, and the polyimide precursor solution was obtained. The solution viscosity of the polyimide precursor solution was 800 poise.

[0043](EXAMPLE)

The porous membrane was manufactured using the device in which the schematic diagram was shown by manufacture drawing 4 of the porous membrane. After obtaining to a polymer feed zone by a reference example, pour into it the polyimide precursor solution which carried out decompression deaeration so that air bubbles may not be involved in, pour in the nitrogen gas which pressurized  $2.5 \text{ kg/cm}^2$ , and with the pressure. The thickness controller cast and adjusted the thickness of the flow casting film to 100 micrometers continuously on the band conveyor made from the stainless steel which drives said polyimide precursor solution with 0.3-m the speed for /through a T die. Using a polyethylene porous membrane (the Ube Industries, Ltd. make, you pore UP2015, air permeability 550 seconds/, 100cc) as solvent substitution speed-regulation material, via the pinch roll, on said flow casting film, substantially, as thickness did not change, it was stuck. These processes were performed under the atmosphere of the temperature of 23 °C, and 50% of relative humidity. Next, the layered product which stuck the band conveyor, the flow casting film, and the polyethylene porous membrane was made to advance into the solidified solution tub in which methanol was stored, the inside of a solidified solution was moved for 5 minutes, it was immersed, and the polyimide precursor porous membrane was deposited. After having led this to the structural stability-ized solvent tub in which water was stored, immersing it from the solidified solution tub with a roll further and coming out of a structural stability-ized solvent tub, it exfoliated and solvent substitution speed-regulation material was removed, it ranked second and the polyimide precursor porous membrane was exfoliated from the band conveyor.

[0044]Next, applying the tension of the grade which a polyimide precursor porous membrane fixes both ends by the pin located in a line at sufficient interval to support a film, and controls crosswise contraction, and controls contraction to a direction of movement. It dried, and a dry tub with a temperature of 80 °C is passed in 10 minutes, a 400 °C heat treatment tub was continuously passed in 20 minutes, heat imide-ization was performed, and polyimide porous membrane was obtained.

[0045]The obtained polyimide porous membrane has flexibility and has 30.0-micrometer uniform thickness.

When methanol was dropped at the surface, it had continuous pores penetrated at the rear face.

When observed with the scanning electron microscope, the average pore size was a high porous membrane with a homogeneity of 0.23 micrometer, and air permeability of the void content was 160 seconds/100cc at 65%.

[0046]The result of having sampled the polyimide porous membrane which carried out continuous fabrication succeedingly every 10 m, and having measured an average pore size and air permeability is shown in Table 1. Average value was [ standard deviation of the aperture ] 0.022 in 0.24 micrometer, and average value was [ standard deviation of air permeability ] 11.0 in 155 seconds/100cc. As for thickness, average value of standard deviation was 1.004 in 29.9 micrometers.

[0047]

[Table 1]

サンプルNo.	平均孔径 ( $\mu\text{m}$ )	透気度 (秒/100cc)	膜厚( $\mu\text{m}$ )
1	0.23	160	30.0
2	0.20	165	29.0
3	0.28	143	29.0
4	0.24	155	31.0
5	0.27	140	29.0
6	0.24	166	30.0
7	0.26	135	31.0
8	0.23	146	29.0
9	0.25	156	28.5
10	0.22	164	29.0
11	0.21	170	31.0
12	0.26	148	32.0
13	0.22	165	30.0
14	0.25	151	30.0
15	0.24	164	30.0
合計値	3.60	2326	448.5
平均値	0.24	155	29.9
標準偏差	0.022	11.0	1.004
変動係数(%)	9.3	7.07	3.36

[0048] In this invention, the aperture of a porous membrane and air permeability were measured by the following method.

\*\* The scanning electron microscope photograph of the average pore size membrane surface of a porous membrane was taken, the punched surface product was measured about the opening of 50 or more points, and it asked for the average diameter at the time of presupposing that pore shape is a perfect circle according to a following formula from the average value of this punched surface product from calculation. Sa of a following formula means the average value of a punched surface product.

Average pore size = it measured according to  $2x(Sa/\pi)^{1/2}$  \*\* air permeability JIS P8117. B type Gurley Denso meter (made by an Oriental energy machine company) was used as a measuring device. The film of a sample is bound tight to 28.6 mm in diameter, and the circular hole of area <sup>2</sup> of 645 mm. With the container liner weight of 567 g, the air in a pipe is passed out of a pipe from an examination circular hole part. Time for 100 cc of air to pass was measured, and it was considered as air permeability (Gurley value).

\*\* The thickness, area, and weight of the film cut off in the void content predetermined size were measured, and the void content was calculated with the following formula from eyes weight. The weight in which S of the following formula measured the membrane area and thickness and w measured d, and D are polymer densities which form this porous membrane, for example, were set to 1.34 with aromatic polyimide.

Void content =  $(1 - W/(S \times d \times D)) \times 100$  [0049]

[Effect of the Invention] Since this invention is what explained above, it does so an effect which is described below. With the continuous production method and continuous fabrication device of a porous membrane of this invention, continuous fabrication of the porous polymer film with the homogeneous porosity characteristics, such as thickness, an aperture, a void content, and pore shape, can be carried out industrially.

[Translation done.]